Anomalous isotope effects of fulleride superconductors

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Abstract

The numerical calculations of the standard Eliashberg-Nambu strong coupling theory and a formula of isotope effect derived in this paper provide direct evidences that an-harmonic vibrations of lattice enhance isotope effect with anomalous coefficient $\alpha > 1/2$. The results in this paper explain very well the wide distributed α values for the samples with different ratios of substitutions of ^{12}C by ^{13}C of fulleride superconductor Rb_3C_{60}. The calculations of isotope effects indicate that the intra-molecule radial modes have more important contributions to superconductivity than the intra-molecule tangential modes with higher phonon frequencies

1 Introduction

The discoveries of isotope effects in metallic superconductors confirm the electron-phonon mechanism as the origin of attractive interaction between

electrons. Anomalous isotope effects such as the negative isotope effects with $\alpha < 0$ and the enhanced isotope effects with $\alpha > 1/2$ are found in many new types of superconductors. Understanding the origin of these anomalous isotope effects is very important to understand the microscopic mechanism of superconductivity.

Coefficient of isotope effect $0 < \alpha < 1/2$ is correct for most conventional superconductors. Negative isotope effect $\alpha < 0$, where T_c increases with mass M, had been found experimentally in conventional superconductors such as PdH [1, 2] ($\alpha = -0.25$), organic superconductors [3, 4] and α-Uranium ($\alpha = -2.0$) [5]. The negative isotope effect had also been found in Sr_2RuO_4 [6] when ^{16}O atoms were substituted by ^{18}O atoms.

Large positive Oxygen isotope effects $\alpha > 1/2$ beyond the BCS value $1/2$ had been found in HTSC material $La_{2-x}Sr_xCuO_4$ (α=0.75) at doping level x=0.12 [7] and in fullerides Rb_3C_{60} ($\alpha > 1.0$) with different ratios of substitutions of ^{12}C with ^{13}C [8, 9, 10]. For $La_{2-x}Sr_xCuO_4$, near x=0.12 the large coefficient of isotope effect is probably due to the strong an-harmonic vibrations companying with structural transitions. Similarly, the transition from partial substitution to completed substitution of ^{12}C by ^{13}C for Rb_3C_{60} leads to the decrease of α from 1.275 or 1.189 [8, 9] to 0.30 [11] because the an-harmonic effect is relatively weak at completed substitution. The Eliashberg theory combined with different models of an-harmonic lattice vibrations had been used to qualitatively explain these anomalous isotope effects [12, 13, 14]. Beyond Migdal's theorem, the coefficient of isotope effect $\alpha > 1/2$ had also been obtained by including non-adiabatic effect [15].

It's very convenient to find a formula for isotope effect which is able to explain anomalous isotope effects such as the enhanced isotope effects with $\alpha > 1/2$ and large negative isotope effect. Most of previous formulas of isotope effects don't include the frequency shift due to the isotope substitution. A formula for isotope effect is derived in this paper using McMillan's T_c formula, which explicitly includes the frequency shift of phonon and is qualitatively consistent with the more accurate numerical results of Eliashberg-Nambu theory. The formula is similar to a previous formula derived with similar idea [16]. In this work, we not only compare the results of the formula with the strong-coupling theory, but also we study in details the meaning of the an-harmonic coefficient A^* and its relation with the potential $V(r)$ of the vibrations of atoms around their equilibrium positions in a crystal. We concentrate on the anomalous isotope effects of fulleride superconductors [17] in the present paper.

An important relation is the key to understand isotope effect and written as

$$M\langle\omega^2\rangle\lambda = \eta = const \qquad (1)$$

where the McMillan-Hopfield parameter η characterizes the chemical environment of atoms in a material [18, 19] and is expressed as $\eta = N(0)\langle J^2\rangle$, where $N(0)$ is the density of state at Fermi energy, J the matrix element of electron-phonon interaction. Certainly, we assume η is constant for isotope substitution or others small structural changes. We will see in section (4) that, under the constraint, the an-harmonic effect is equivalent to the fact that the parameter λ is dependent on M the mass of atom. In a previous work, using electron-phonon mechanism and the constraint Eq.(1), we have successfully explained the spatial anti-correlation of the energy gap and the phonon energy of Bi2212 superconductors observed in STM experiments [20]. In this work, using the constraint combining with McMillan's T_c formula, we derive a formula of isotope effect that can explain almost all anomalous isotope effects, especially for fulleride superconductors.

2 Theory

The energy-gap equation of Eliasgberg-Nambu theory in the Matsubara's imaginary energy form is standard [18]. When temperature is very close to transition temperature T_c, the Eliashberg equation can be simplified as

$$\sum_{n=0}^{N}(K_{mn} - \rho\delta_{mn})\bar{\Delta}_n = 0 \quad (m \geq 0) \qquad (2)$$

$$K_{mn} = \lambda(m-n) + \lambda(m+n+1) - 2\mu^*(N)$$
$$- \delta_{mn}(2m+1+\lambda(0)+2\sum_{l=1}^{m}\lambda(l)),$$

where $\bar{\Delta}_n = \Delta_n/|\omega_n|$ is the energy-gap parameter and $\lambda(n) = 2\int_0^\infty d\omega\alpha^2F(\omega)\omega/(\omega^2+(2\pi nT)^2)$. The pair-breaking parameter ρ is introduced to form a eigenvalue problem with $\rho=0$ corresponding the physical energy-gap equation. The transition temperature T_c is defined as the temperature when the maximum of eigenvalue of kernel matrix K_{mn} crosses to zero and changes its sign. We use about N=200 Matsubara energies to solve above equation.

The Eliashberg function is expressed as

$$\alpha^2 F(\omega) = \begin{cases} \frac{c}{(\omega - \Omega_P)^2 + (\omega_2)^2} - \frac{c}{(\omega_3)^2 + (\omega_2)^2}, & |\omega - \Omega_P| < \omega_3 \\ 0 & \text{others,} \end{cases} \quad (3)$$

where Ω_P is the energy (or frequency) of phonon mode, ω_2 the half-width of peak of phonon mode and $\omega_3 = 2\omega_2$. We can write the parameter of electron-phonon interaction $\lambda = \lambda(0) = 2\int_0^\infty d\omega \alpha^2 F(\omega)/\omega$. The moments $\langle \omega^n \rangle$ of the distribution function $(2/\lambda)\alpha^2 F(\omega)/\omega$ are defined as $\langle \omega^n \rangle = 2/\lambda \int_0^\infty d\omega \alpha^2 F(\omega)\omega^{n-1}$. The parameter λ characterizes the strength of electron-phonon interaction by $\lambda \propto N(0)\langle J^2 \rangle/M\langle \omega^2 \rangle$ in terms of Eq.(1). The Coulomb pseudo-potential is defined as $\mu_0 = N(0)U$ and its renormalized value as $\mu^* = \mu_0/(1 + \mu_0 \ln(E_C/\omega_0))$, where U is the Coulomb parameter, E_C the characteristic energy for electrons such as the Fermi energy or band width, and ω_0 the characteristic phonon energy such as the energy cutoff of phonon energy or Debye energy. If $\omega_2 \ll \Omega_P$, Eq.(1) can be simplified as

$$M\Omega_P^2\lambda = \eta = const, \quad (4)$$

which is obviously correct for Einstein model $\alpha^2 F(\omega) = (\lambda/2)\Omega_P \delta(\omega - \Omega_P)$.

3 A formula of coefficient of isotope effect

We will derive a formula of isotope effect by including an-harmonic effect. The shift of phonon energy (or frequency) is explicitly included in the formula. For single-frequency like mode, the α values in terms of the formula are qualitatively consistent with the numerical solutions of Eliashberg equation. Most importantly, the formula clearly shows that the an-harmonic vibration of lattice leads to the enhanced isotope effect with $\alpha > 1/2$. It's conveniently to define a parameter A^* by $\Omega_P \propto M^{-(1-A^*)/2}$ to measure the an-harmonic effect. We can easily see that $A^* \neq 0$ represents the an-harmonic effect. The an-harmonic parameter A^* can be expressed as

$$A^* = 1 + 2M/\Omega_P(\delta\Omega_P/\delta M). \quad (5)$$

Under harmonic approximation $\Omega_P \propto M^{-1/2}$, the parameter λ is a constant $(\delta\lambda/\delta M = 0)$ because

$$A^* = 1 + 2M/\Omega_P(\delta\Omega_P/\delta M) = -M/\lambda(\delta\lambda/\delta M) = 0$$

by using the relation $M\Omega_P^2\lambda = const.$

We start from the McMillan formula of transition temperature T_c of superconductor

$$T_c = \frac{\Theta_D}{1.45} \exp[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}].$$

(6)

where λ is the strength of electron-phonon interaction. The coefficient α of isotope effect defined by $T_c \propto M^{-\alpha}$ can be obtained from above McMillan formula by the direct mass-dependent from $\Theta_D \propto M^{-1/2}$ and implicit mass-dependent from μ^* by $\omega_0 \propto M^{-1/2}$. If an-harmonic effect is included then $\Theta_D, \omega_0 \propto M^{-(1-A^*)/2}$. In this work we consider additionally mass-dependent from λ by the well known constraint $M\Omega_P^2\lambda = \eta$, we obtain a formula of isotope effect which is expressed as

$$\alpha = \frac{1}{2} - \frac{1.04(1+\lambda)(1+0.62\lambda)(\mu^*)^2}{2[\lambda - \mu^*(1+0.62\lambda)]^2} + A^*T(\lambda, \mu^*)$$

(7)

where A^* is defined in Eq.(5) and the function $T(\lambda, \mu^*)$ is expressed as

$$T(\lambda, \mu^*) = \frac{1.04\lambda(1+0.38\mu^*)}{[\lambda - \mu^*(1+0.62\lambda)]^2}$$

(8)

or

$$T(\lambda, \mu^*) = \frac{\lambda(2.08 - \lambda) + \lambda(2.7904 + 1.24\lambda)\mu^*}{2[\lambda - \mu^*(1+0.62\lambda)]^2}$$
$$+ \frac{(0.04 + 0.42\lambda)(1+0.62\lambda)(\mu^*)^2}{2[\lambda - \mu^*(1+0.62\lambda)]^2},$$

(9)

dependent on whether $\Theta_D, \omega_0 \propto M^{-1/2}$ for Eq.(8) or $\Theta_D, \omega_0 \propto M^{-(1-A^*)/2}$ for Eq.(9). We notice that, for the Eq.(8), the an-harmonic effect enters into the coefficient α only by the M-dependent λ, however for the Eq.(9) not only by M-dependent λ but also by the Θ_D and ω_0. It's very important that $T(\lambda, \mu^*) > 0$ for reasonable values $0 < \lambda < 2 < 2.08$, so the sign of the third term of Eq.(7) is determined by the an-harmonic parameter A^*. It's obviously that $A^* = 0$ under harmonic approximation $\Omega_P \propto M^{-1/2}$ and the third term in the Eq.(7) is also zero. The derivative $\delta\Omega_P/\delta M$ used in the calculation of an-harmonic parameter A^* is approximately obtained from the experimental energy (or frequency) shift of phonon. The first two terms give $\alpha < 1/2$. The properties of the third term to isotope effect is determined

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by the sign of the an-harmonic parameter A^*. Generally, Ω_P decreases with increasing mass M, thus $2(M/\Omega_P)\delta\Omega_P/\delta M < 0$. If $2|(M/\Omega_P)\delta\Omega_P/\delta M| < 1$, $A^* > 0$. So we can get $\alpha > 1/2$ if the third term has larger absolute value than the second term.

4 The anomalous isotope effects with $\alpha > 1/2$

In many literatures of $A_n C_{60}$, the average mass m of C_{60} is used in the definition of coefficient of isotope effect by $\tilde{\alpha} = -(m/T_c)\delta T_c/\delta m$. If the ratio of substitution is p, the average mass of C_{60} molecule $m = 60[M_{12}(1 - p) + M_{13}p]$, so $\delta m = m - 60M_{12} = 60p\delta M$ with $\delta M = M_{13} - M_{12}$. The relation $\tilde{\alpha} = \alpha/p$ connects the parameter $\tilde{\alpha}$ with the usual definition of $\alpha = -(M/T_c)(\delta T_c/\delta M)$. The usual coefficient of isotope effect $\alpha = p\tilde{\alpha} = 1.275$ is obtained with $\tilde{\alpha}$=2.125 and p=0.60 [8], $\alpha = 1.189$ with $\tilde{\alpha}$=1.45 and p=0.82 [9], $\alpha = 0.462$ with $\tilde{\alpha}$=1.4 and p=0.33 [10]. For completed substitution with p=1.0, $\alpha = \tilde{\alpha}$=0.30 [11].

The relation $M\langle\omega^2\rangle\lambda = \eta = const$ services as a constraint to determine the parameters λ and Ω_P in numerical calculations. The Coulomb pseudo-potential μ^* has to change in isotope substitution because μ^* is dependent on the cutoff of phonon energy $\omega_0 \propto M^{-1/2}$ or $\propto M^{-(1-A^*)/2}$ in an-harmonic approximation. In harmonic approximation, $\delta\mu^* = -(\mu^*)^2\delta M/2M$, the an-harmonic effect is included in calculations only by the M-dependent λ. The an-harmonic effect can be realized by shifting phonon energy $\delta\Omega_P$ to make $A^* = 1 + 2M/\Omega_P(\delta\Omega_P/\delta M) \neq 0$.

The intra-molecule radial mode, which is about Ω_P=65 meV or 525 cm^{-1} from infrared spectrum [10, 8] and the intra-molecule tangential modes around 1400^{-1} or 174 meV [17] have strong intensity. However we concentrate attentions on the intra-molecule radial mode with energy Ω_P=65 meV and half-width ω_2=8 meV. The Coulomb parameter $\mu_0 = UN(0)$ and the corresponding renormalized Coulomb parameter $\mu^* = \mu_0/[1+\mu_0 \ln(E_C/\omega_0)]$ can be estimated from ab-initio density functional theory (DFT) based on pseudo-potential method using atomic orbital basis functions[21]. In the DFT calculation, the super-cell includes one C_{60} molecule and three Rb atoms. The effect of orientation of different C_{60} molecules is ignored. The parameter U is the charge energy defined as $\delta^2 E_{tot}/\delta n^2 = E(n+1)+E(n-1)-2E(n)$, $E(n)$ the total energy of electric-neutral system of n valence electrons, $E(n + 1)$ and $E(n - 1)$ the total energies with one negative and one positive charge

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Table 1: The Coulomb parameter μ^* is calculated when we choose valence-electron configuration (a) $4p^6 5s^1$ for Rb atom and $2s^2 2p^2$ for Carbon atom in DFT calculations. The case (b) is corresponding to the general value μ^*=0.10. The coefficients α of isotope effects are calculated using the phonon-energy shifts from 65 meV to 62.3 meV after the isotope substitution (A^*=0.003).

	U(eV)	N(0)(1/eV)	UN(0)	$\ln(E_F/\omega_0)$	μ^*	λ	T_c(K)	α
(a)	1.991	2.197	4.374	6.9078	0.127	0.700	29.544	0.342
(b)					0.100	0.670	29.820	0.358

respectively. We choose the possible valence-electron configuration $4p^6 5s^1$ for Rb atoms and $2s^2 2p^2$ for Carbon atoms. The core electrons are presented by Troulier-Martins pseudo-potentials. The electrons in semicore state 4p of Rb atoms having already treated as valence electrons have the single-ζ basis set and all others valence electrons for all atoms have the split valence double-ζ plus polarized basis sets. We use Γ point sampling the first Brillouin zone. The exchange-correlation potential is GGA Perdew-Burke-Ernzerhof type[22] and the spin-polarization effects are included in the self-consistent calculations. The results in table(1) show that the Coulomb parameter μ_0 is equal to 4.374 and the renormalized Coulomb parameters μ^* is 0.127 if the maximum of phonon energy ω_0 is 150meV and E_C=15 eV when all valence electrons are included. The common value μ^*=0.10 is close 0.127 obtained in this work. We have known the Coulomb parameter μ^* and the phonon energy Ω_P, the parameter λ of electron-phonon interaction can be defined by the experimental transition temperature. From table(1), we can see that the parameters μ^* have small influence on isotope effects. Below we present the calculations of coefficient α of isotope effects with μ^*=0.1.

The parameter of electron-phonon interaction λ=0.67 is defined by the experimental transition temperature T_c about 29.5(K) using parameters μ^*=0.1 and Ω_P=65 meV. We calculate the $\eta = \eta_{12}$ for ^{12}C. The phonon energies after ^{13}C substitutions are unknown because the phonon energies are dependent on the ratios of ^{13}C substitutions. We choose the nine possible energies for phonons in table (2), which are all smaller than Ω_P=65 meV because the energies (or frequency) decrease with increasing mass of atoms. We also assume that the parameters λ of electron-phonon interaction alter after isotope substitutions. The new Eliashberg function $\alpha^2 F(\omega)$ after isotope

Table 2: The simulation parameters and the results with different an-harmonic parameters A^*. The coefficients α are calculated based on the numerical solutions of Eliashberg equation and α' from the formula Eq.(7) and Eq.(8) derived in this paper.

^{13}C	M (u)	Ω_P (meV)	λ	T_c (K)	A^*	α	α'
(1)	13	64.3	0.632	25.5	0.742	1.929±0.10	2.377
(2)	13	63.4	0.650	27.2	0.409	1.207±0.09	1.516
(3)	13	62.3	0.674	29.0	0.003	0.358±0.09	0.464
(4)	13	62.2	0.676	29.2	-0.034	0.282±0.09	0.368
(5)	13	62.0	0.680	29.5	-0.108	0.132±0.08	0.177
(6)	13	61.8	0.685	29.8	-0.182	-0.02±0.08	-0.014
(7)	13	61.6	0.689	30.3	-0.255	-0.165±0.08	-0.205
(8)	13	61.2	0.698	30.9	-0.403	-0.457±0.08	-0.588
(9)	13	60.0	0.727	33.2	-0.846	-1.305±0.08	-1.736
^{12}C	12	65.0	0.670	29.82			

substitution by ^{13}C is obtained from the old one before isotope substitution by simply shifting energy of phonon and scaling it to satisfy the constraint $M\langle\omega^2\rangle\lambda = \eta_{13} = \eta_{12}$. Based on the new Eliashberg function $\alpha^2 F(\omega)$, we can calculate the T_c and λ after the isotope substitution. The new Coulomb pseudo-potential after isotope substitution $\mu^*=0.099583$ is obtained from the formula $\delta\mu^* = -(\mu^*)^2\delta M/2M$. The nine possible values of λ corresponding to nine possible energies of phonon are collected in table (2). The transition temperatures T_c are obtained by solving Eliashberg equation Eq.(2). The coefficients α are easily calculated in terms of the transition temperatures T_c after and before isotope substitutions by $\alpha = -\ln(^{13}T_c/^{12}T_c)/\ln(M_{13}/M_{12})$. The an-harmonic parameters A^* are calculated in terms of the shifts of phonon energies.

For the case (2) in table (2), we get $\alpha = 1.207$ which is very close to the already known maximum value 1.275 in experiments with uncompleted substitution ($\tilde{\alpha}$=2-2.25, p=0.60) [8]. For sample with completed substitution with ^{13}C, the value of α decreases to ~0.30 [11]. To explain the interesting results, we assume the increase of ratio of substitution makes the distribution of ^{13}C more homogenous and the an-harmonic effect become weak with small A^*. If the phonon energy shifts to 62.3 meV with smaller an-harmonic parameter A^*=0.003, the value of α=0.358 is close to the experimental values
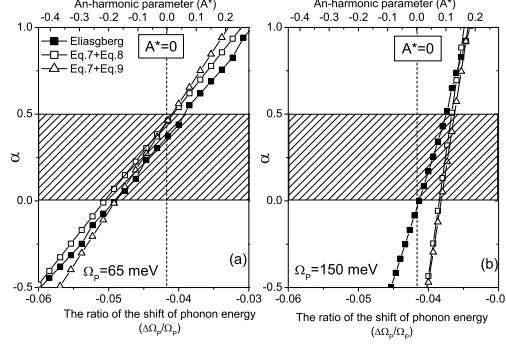
Figure 1: The comparison of coefficients of isotope effect having obtained from numerical calculations of Eliashberg equation and from Eq.(7) for radial intra-molecule mode Ω_P=65 meV (a) and the tangential intra-molecule mode Ω_P=150 meV (b)

from 0.30 to 0.37 for the samples with completed substitution.

For negative an-harmonic parameterA^*=-0.182, we find α=0.02 close to zero. After having made A^* more negative further, at A^*=-0.403, we get the negative coefficient α=-0.457. However, the negative isotope effect wasn't found in fulleride superconductors. From above calculations we can see that the sign of A^* determines the sign of α at relative larger absolute values of A^*. If the absolute values of an-harmonic parameters are not too large $0.07 > A^* > -0.21$ or an-harmonic effect is weak, the coefficient α are from 0 to 0.5 within the range of general values. The above calculations explain the wide distributed values of coefficients for Rb_3C_{60} in experiments. This is because the an-harmonic parameters are dependent on the ratios of substitutions.

From table (2), we can see that the values obtained from numerical calculations are very close to the values from Eq.(7) with Eq.(8). The values of α and α' have the same sign on the same rows. It's very important that if $\alpha > 1/2$, $A^* > 0$ must be satisfied. Thus, the enhanced coefficients α larger than $1/2$ for Rb_3C_{60} in uncompleted substitution samples mean that the strong an-harmonic effects. If the an-harmonic effect becomes weak as approaching the completed substitution, the value of α will decrease and reach to smaller value about 0.358 at $A^* = 0.003$.
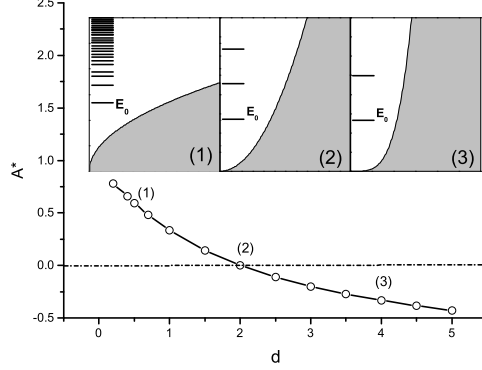
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Figure 2: An-harmonic coefficients A^* for the models of interaction with form $V(r) = hr^d$. The inserted figures (1),(2) and (3) illustrate the shapes of interacting potentials and the quantized energy levels for h=0.01 and d=0.5, 2.0 and 4.0 respectively. The maximum of quantum number of angular momentum is up to l_{max}=8

Fig. 1(a) shows the results of the numerical solutions of Eliashberg equation and the formula Eq.(7). We can see that Eq.(7) with Eq.(8) is more close to the numerical solution than using the Eq.(9) although for Eq.(9) more completed an-harmonic effects are included. We have preformed the same calculations for intra-molecule tangential mode with energy Ω_P=150 meV, μ^*=0.285, λ=0.67 and T_c=29.5(K). From Fig.1(b), there is larger slope of α-$\delta\Omega_P/\Omega_P$ curve compared with the intra-molecule radial mode with energy Ω_P=65 meV. The coefficient of isotope effect of the intra-molecular radial mode α=0.358 at $A^* \simeq 0.0$ is more close to experiments at completed substitutions $\alpha \sim 0.30 - 0.37$. So it is more correlated with superconductivity of fulleride than the intra-molecule tangential mode.

5 An-harmonic parameter A^* and models of lattice vibrations

In this paper, we introduce an important parameter, the an-harmonic parameter A^*. To make parameter A^* more realistic, we study the models of lattice

vibrations in a crystal. The atoms in crystal move around their equilibrium positions. The change of potential energy of an atom away from its equilibrium position is written as $V(r) = hr^d$ with radially local displacement r. The harmonic vibration is corresponding $d = 2$. We had numerically solved the Schrödinger equation $[-\hbar^2 \nabla^2 / 2M + V(r)] \psi(\vec{r}) = E \psi(\vec{r})$ under isotropic approximation, especially, the one-dimensional radial part converts into difference equation. We calculated the relation $E_0(M)$ between energy of ground state and mass of atom for a series of discrete values of M. It's well known that for harmonic approximation $E_0(M) \propto 1/M^{0.5}$. The effective an-harmonic parameters A^* for interaction with the form $V(r) = hr^d$ are obtained by fitting the discrete $E_0(M)$ functions with function $\tilde{E}_0(M) \propto 1/M^{(1-A^*)/2}$. From the Fig.2, if $d < 2$ we can obtain $A^* > 0$. So the enhanced isotope effects with $\alpha > 0.5$ are hopefully found based on the formula Eq.(7) obtained in this work. If $d > 2$ so $A^* < 0$, we can get the normal isotope effects with $\alpha < 0.5$ and the negative isotope effects with $\alpha < 0$. We can see that the simple model $V(r) = hr^d$ is suitable for the isotope effects of fulleride Rb_3C_{60} for different ratios of substitutions because the an-harmonic parameters are within the range to obtain experimental values of α.

6 Discussion and Summary

The Figure 1(b) shows clearly that the formula Eq.(7) isn't good approximation to more accurate numerical solution for high-energy mode. The reason is probably that McMillan's formula isn't correct in some regions of parameter space. The McMillan's formula is good approximation when the parameter λ of electron-phonon interaction is not too large ($\lambda < 1$) and the phonon energy Ω_P is not too high. The inter-molecule phonon modes such as the vibration between C_{60} molecules and the between alkali-metal atoms and C_{60} molecules are ignored in this work because their energies generally smaller than 12 meV. To obtain T_c=30K, the parameters λ of electron-phonon interaction are at least 3.0 so the instability of lattice will destroy superconductivity. However, these inter-molecule modes still have significant influence on the properties of fulleride superconductors such as the differences of isotope effects for different substitution configurations $Rb_3[(^{13}C_{60})_x(^{12}C_{60})_{1-x}]$ and $Rb_3(^{13}C_x^{12}C_{1-x})_{60}$ [11].

In summary, the coefficients α of isotope effects obtained in this paper are very close to the values in experiments or within the range of experimental

values. The reductions of α with increasing the substitution ratios of ^{13}C are due to the reductions of an-harmonic effects of lattice vibrations when the ratios of substitution tend to 100%. The enhanced coefficients of isotope effects with $\alpha > 1/2$ generally happen at the intermediate stage of transition from one phase to another. Finally, the formula Eq.(7) and the numerical methods used in this paper are also suitable to study isotope effects of other superconductors if the electron-phonon interaction is the pairing mechanism for electrons.

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